On the Fluorescence of Iodine Vapour Excited by Ultra-Violet Light.

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[PLATE 1.]

I. *Introduction.*

In a recent communication* by the writer a new fluorescence spectrum of iodine vapour was described which could be stimulated by the light from the mercury arc. This fluorescence spectrum consisted of a set of narrow bands extending from λ 4600 down to λ 2100. While the whole of this spectrum was clearly defined, the most intensely marked portion of it was made up of a set of seven equally spaced bands between λ 3315 and λ 3175. In obtaining the spectrum a highly exhausted tube of fused quartz containing a few iodine crystals was inserted axially in an ordinary glass Cooper-Hewitt mercury arc lamp, with a lateral anode and provided with a short extension at the positive end, to which the quartz tube was sealed with mastic wax. The quartz iodine vapour tube was provided with a window of clear fused quartz, towards which the collimator of a quartz spectrograph was directed in taking the photographs. When the Cooper-Hewitt tube was in action the arc played directly upon the inserted quartz tube and so subjected the vapour contained in it to intense illumination.

In the paper describing this fluorescence spectrum of iodine vapour it was pointed out that it was impossible to obtain the spectrum when the inserted tube containing the iodine vapour was made of combustion glass tubing. It was also pointed out that this glass tubing was found to be transparent to the light from the mercury arc down to λ 2893·7, and on account of this fact the conclusion was drawn that the light which stimulated the iodine vapour to the fluorescence referred to must have had a shorter wave-length than λ 2893·7.

The present communication contains the results of experiments made to determine the range of the exciting light, together with a statement of some points of interest in connection with the fluorescence spectrum which developed while these experiments were being made.

* 'Roy. Soc. Proc.,' A, vol. 88, p. 289 (1913).

II. *The Effect of Temperature.*

In order to ascertain, approximately at least, the temperature at which the iodine vapour was maintained when it emitted the fluorescence spectrum with the experimental arrangements described above, the projecting end of the quartz tube containing the vapour was cut off and one of the terminals of a nickel-iron thermo-couple was inserted. When the Cooper-Hewitt lamp was put into action this terminal was shoved along in the tube to different positions and the thermo-electromotive force developed at each position was noted. The details of this investigation have been described elsewhere* but the chief point of interest here is that at all points along the tube where the latter was directly in contact with the arc it was found that under the conditions of the experiment the temperature was always within two or three degrees of 326° C.

This explains the absence from the plates of any trace of the resonance spectra which, as Wood has so beautifully shown, iodine vapour emits when the light of the yellow and green lines of the mercury arc is allowed to fall upon it ; for in a communication from him to the writer he states that such resonance spectra are no longer emitted when the vapour is raised to a moderately high temperature.

Further experiments showed that iodine vapour could be made to emit its fluorescence spectrum under stimulation by the light from the mercury arc at room temperatures as well as at the temperature 326° C. To show this, some iodine crystals were placed in a tube of clear fused quartz 3·5 cm. in diameter and about 60 cm. in length. The tube was then placed alongside of a Cooper-Hewitt mercury arc lamp, also made of fused quartz. When this lamp was put into action, and the light emitted by the iodine tube through one of its ends examined with a quartz spectrograph, it was found to give both Wood's resonance spectra and the fluorescence spectrum described by the writer. With a set of lighted Bunsen burners placed beneath the iodine tube, and the latter raised to a red heat, the resonance spectra once more disappeared from the photographs, but the fluorescence spectrum remained, with no apparent diminution in intensity. It was therefore evident that, while the resonance spectra could only be obtained at comparatively low temperatures, the fluorescence spectrum could be obtained from the iodine vapour over the whole range of temperatures from that of the room up to about 1000° C.

* 'Roy. Soc. Canada Proc.,' May, 1913.

III. *Excitation Region.*

In attempting to locate the range of wave-lengths of the light which stimulated the iodine vapour to fluorescence, the apparatus shown in fig. 1 (Plate 1) was used. AB was an inner tube of fused quartz and CD an outer one of the same material. The diameter of the inner tube was about 2 cm., and the space between the inner and the outer tube was about 5 mm. The inner tube, which was highly exhausted, contained the iodine vapour. When this double tube was placed alongside of the quartz Cooper-Hewitt mercury lamp in action, it was found that the iodine was stimulated to fluorescence when the space between the two tubes was filled with air or oxygen at atmospheric pressure or with distilled water, but not when it was filled with glycerine. With the latter substance, however, the spectrograms showed that light down as far as $\lambda\,2340$ entered the iodine tube. The light which stimulated the iodine to fluorescence must therefore have been of a still shorter wave-length than $\lambda\,2340$. In seeking for a lower limit to the region of excitation, it was not found possible to determine it very definitely. Layers of fused quartz and of water, each 5 mm. in thickness, were both found to be still transparent to light as short as $\lambda\,1849$ in wave-length. Lyman[*] has shown that crystal quartz is not transparent to light of shorter wave-length than $\lambda\,1600$, and it is probable that this may be taken as the limit of transparency for fused quartz as well.

Lyman[†] has also shown that air at atmospheric pressure has a strong and wide absorption band beginning at $\lambda\,1710$, and oxygen, at the same pressure, a band beginning at $\lambda\,1760$. As there was always an air space between the lamp and the iodine tube of from 3 to 4 cm., it is clear that the light which caused the fluorescence must have been of longer wave-length than $\lambda\,1760$. The experiments described so far, therefore, show that the excitation region lay between $\lambda\,2340$ and $\lambda\,1760$. As the strong lines in the mercury arc spectrum in this region are given by Handke[‡] and by Wolff[§] as $\lambda\,1942{\cdot}3$ and $\lambda\,1849{\cdot}6$, it appeared that the fluorescence was excited by the light of one or both of these lines.

To test the matter still further, a series of photographs was taken with a small quartz spectroscope, with its slit close to the quartz mercury lamp. In all these photographs the line $\lambda\,1942{\cdot}3$ came out quite clearly, but no trace of the line $\lambda\,1849{\cdot}6$ was obtained. This, as Kirschbaum's[||]

[*] Lyman, 'Astrophys. Journ.,' vol. 25, No. 1, p. 45 (Jan., 1907).

[†] Lyman, 'Astrophys. Journ.,' vol. 27, No. 3, p. 87 (March, 1905).

[‡] Handke, 'Untersuch. im Geb. der Schumannstrahlen,' Berl., Diss., 1909.

[§] Wolff, 'Ann. der Phys.,' vol. 42, p. 825 (1913).

[||] Kirschbaum, 'Electrician,' vol. 72, p. 1074 (1914).

later experiments have shown, was due to the fact that the light of this wave-length is strongly absorbed by mercury vapour. The comparatively cool layers of mercury vapour in the lamp close to its walls, therefore, must have acted as an absorbing screen, and so prevented the light of that wave-length from getting out of the lamp tube with sufficient intensity to affect the photographic plates. From these experiments it would appear, then, that the light from the mercury arc which stimulated the iodine to fluorescence was chiefly that of wave-length λ 1942·3.

Further experiments were made which showed that the fluorescence of iodine vapour could be excited by light from the mercury spark in air as well as by that from the mercury arc. In these, two tubes of ordinary silica tubing were sealed into two iron cups, and were then fastened to a support, with their lower ends some distance apart and with their upper ones close together. The tubes were filled with mercury and the iron cups were connected to the two terminals of an induction coil with two half-gallon Leyden jars in parallel. In spectrograms taken with this form of mercury spark, the line λ 1849·6 came out quite clearly, and the line λ 1942·3 was much stronger than it was on the plates taken with the mercury arc.

With the mercury spark placed close to the iodine tube, it was found that the fluorescence was considerably stronger than it was when the mercury arc was used to stimulate the vapour.

After it was found that fluorescence could be excited in the iodine vapour by the light from the mercury spark, the light from the spark between terminals of a number of other metals was tried. These included aluminium, zinc, cadmium, and magnesium, and with all of them it was found that strong fluorescence was excited. This made it clear that it was not necessary for the exciting light to be of one definite wave-length, and that it sufficed if the light was confined to a portion of the spectrum lying somewhere near λ 1942 and between λ 2340 and λ 1760.

In order to determine within narrower limits if possible the excitation range of wave-lengths, some additional experiments were made with the tube shown in fig. 1, in which mixtures in different proportions of glycerine and water were used as absorbing screens. When a screen of 5 parts water to 1 of glycerine was used it allowed the light from the zinc spark corresponding to λ 2063 to enter the iodine tube, but cut off the line λ 2026 and all below it. With an aluminium spark this screen also cut off the light corresponding to the strong line λ 1990, as well as all light from that source of still shorter wave-length. However, when this 1 to 5 glycerine-water screen was used and the light from the aluminium, the

zinc, the cadmium, or the mercury spark was allowed to fall upon the tube, it was found that the fluorescence spectrum always came out, though very faintly, on the plates. In these experiments the exciting light must have belonged to wave-lengths between λ 2340 and λ 2063, and as the fluorescence obtained under these circumstances was faint, it would go to show that the excitation range of wave-lengths began somewhere near λ 2100. It was found impossible with the resources available to ascertain with any exactness the lower limit to the excitation region, but it may be of interest to point out that although the iodine vapour was exposed for 26 hours to the γ-rays from 30 mgrm. of pure radium bromide, and also later for two hours to the strongest Röntgen rays, no photographic indication of fluorescence was obtained.

From the fact that very strong fluorescence was obtained with light from the aluminium and mercury sparks, and the fact that the spectra of these metals both include a strong line between λ 1900 and λ 2000, it would seem that the maximum of the excitation range of wave-lengths was somewhere between these limits.

As the bands constituting this fluorescence spectrum began at about λ 4600 and were detectable down to about λ 2100 it would seem from what has gone before that we have to do here with a case of ordinary fluorescence where Stokes' law is followed and where fluorescence is stimulated by the light from any one of a number of wave-lengths of a limited portion of the spectrum.

Further, it is clear that this ultra-violet fluorescence spectrum of iodine vapour is entirely different in its characteristics from the resonance spectra obtained by Wood with iodine vapour, for (as he has shown) the constitution of each of these resonance spectra is determined by and depends solely upon exciting light of a single wave-length.

IV. *Fluorescence of the Vapours of Iodine Compounds.*

When working with the original form of apparatus in which the iodine tube was inserted axially in a Cooper-Hewitt lamp and exposed directly to the light of the mercury arc, experiments were made to see if the vapours of a number of the compounds of iodine could be stimulated to fluorescence. None was obtained with zinc, bismuth, or phosphoric iodide, but with both iodoform and mercuric iodide a fluorescence spectrum was obtained which contained the seven well-marked bands of the iodine vapour fluorescence spectrum between λ 3315 and λ 3175.

The fluorescence spectrum of mercuric iodide, however, differed from that of iodine vapour in that it possessed some special characteristics of its own.

It contained a set of five narrow well marked bands or lines between λ 3130 and λ 3020, a set of fine lines, less well marked, between λ 3020 and λ 2923, and also a set of fine lines extending from λ 4359 to λ 3660. It contained besides two broad fluorescent bands with their centres approximately at λ 3440 and λ 3280 respectively. In addition to the seven well marked lines of the iodine vapour fluorescence spectrum referred to above, the fluorescence spectrum of iodoform also contained the bands of the iodine fluorescence spectrum between λ 4290 and λ 3625, but no others. The fluorescence spectrum of iodoform differed from that of mercuric iodide in that it did not contain any characteristic bands or lines of its own.

With potassium iodide a fluorescence spectrum was obtained which did not contain any of the bands of the iodine vapour fluorescence spectrum. It consisted, however, of two sets of unequally spaced fine lines, the one set lying in that portion of the spectrum between λ 4047 and λ 3340, and the other in the portion between λ 3075 and λ 2940.

V. *Resonance Spectra of Iodine Vapour.*

An attempt was made with the tube shown in fig. 1 to see if iodine vapour could be stimulated to the emission of resonance spectra other than those produced by the light from the mercury arc of wave-lengths λ 5790·66, λ 5769·6 and λ 5460·74. The space between the two tubes was filled with glycerine to prevent the ultra-violet fluorescence of the iodine vapour, and the tube was placed alongside of and close to a long quartz Cooper-Hewitt mercury arc lamp in action. Although a number of photographs were taken with the quartz spectrograph of the light issuing from the end of the iodine tube, none of them contained lines other than those of the mercury spectrum and the lines of the resonance spectra excited by the light of the three mercury lines mentioned above. None of the lines of the mercury spectrum below λ 5460·74 and down to λ 2340 gave any indication of possessing the capacity in any degree of exciting the iodine vapour to the emission of a resonance spectrum. From this result it is evident that resonance spectra of any considerable intensity can be obtained from iodine vapour only when the latter is subjected to a stimulation by light confined to a narrow portion of the spectrum in the neighbourhood of the yellow and green lines of mercury.

VI. *Summary of Results.*

(1) It has been shown that iodine vapour can be stimulated to the emission of a fluorescence spectrum excited by ultra-violet light at temperatures ranging from room temperature to at least as high as 1000° C.
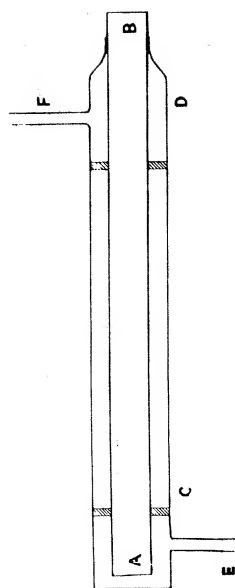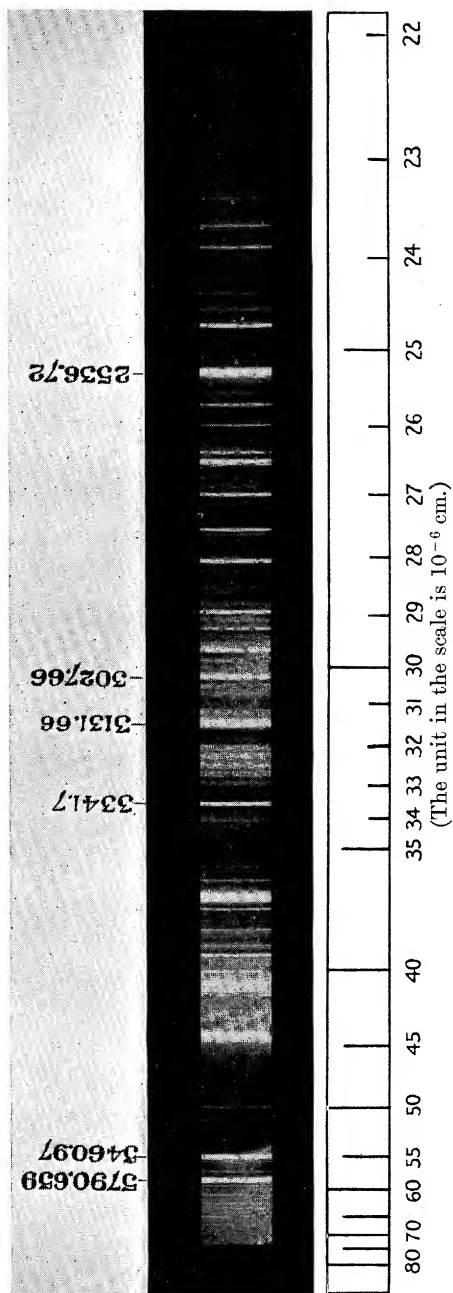
FIG. 1.

(The unit in the scale is 10^{-6} cm.)

FIG. 2.

(2) Iodine vapour ceases to be capable of emitting the resonance spectra discovered by Wood at some temperature below 326° C.

(3) The wave-lengths of the light which can stimulate the ultra-violet fluorescence of iodine vapour lie between λ 2100 and a lower limit probably about λ 1800.

(4) Resonance spectra cannot be obtained with iodine vapour when illuminated with light from the mercury arc of wave-length shorter than that of λ 5460·74.

(5) Portions of the ultra-violet fluorescence spectrum of iodine vapour were obtained with iodoform and mercuric iodide at a temperature of about 326° C.

(6) Mercuric iodide and potassium iodide at a temperature of about 326° C. were shown to exhibit characteristic fluorescence spectra of their own when excited by light from the mercury arc.

In conclusion the writer desires to acknowledge assistance received from Mr. P. Blackman and Mr. F. Mezen throughout the investigation.

EXPLANATION OF PHOTOGRAPH.
(PLATE 1, FIG. 2.)

The reproduction shows, in addition to the lines of the mercury arc, the bands of the ultra-violet fluorescence spectrum of iodine vapour and the lines of Wood's resonance spectra. It was taken by exposing iodine vapour in a highly exhausted tube of fused quartz to the light emitted by a fused quartz Cooper-Hewitt mercury arc lamp. The lines of the resonance spectra lie beyond λ 5790·659. The fluorescence bands are well marked between λ 3341·7 and λ 3131·66, and can also be seen in the background both above and below these two limits.

FIG. 1.

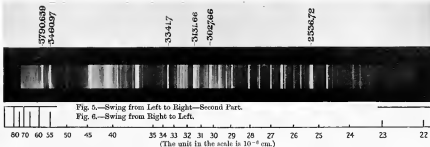| 37500680 3549097		33417	3136166	3005766		21504272

Fig. 5.—Swing from Left to Right—Second Part.
Fig. 6.—Swing from Right to Left.

(The unit in the scale is 10^{-8} cm.)

FIG. 2.

EXPLANATION OF PHOTOGRAPH.

(PLATE 1, FIG. 2.)

The reproduction shows, in addition to the lines of the mercury arc, the bands of the ultra-violet fluorescence spectrum of iodine vapour and the lines of Wood's resonance spectra. It was taken by exposing iodine vapour in a highly exhausted tube of fused quartz to the light emitted by a fused quartz Cooper-Hewitt mercury arc lamp. The lines of the resonance spectra lie beyond λ3700′655. The fluorescence bands are well marked between λ3341·7 and λ3131·66, and can also be seen in the background both above and below these two limits.